ENHANCED BIOREMEDIATION OF A BTEX CONTAMINATED SOIL IN BELGIUM

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Abstract

Biodegradation of organic contaminants in soil is often limited by the availability of oxygen. The injection of oxygen releasing chemicals can be a cost effective remediation option for relatively low BTEX (Benzene, Toluene, Ethlybenzene, Xylene) concentrations in groundwater (<20 mg/L).

IXPER® 75C Calcium Peroxide was chosen as oxygen releasing chemical over magnesium peroxide and sodium percarbonate due to its high oxygen availability and its slow and extended release of oxygen. During 18 months, stimulated aerobic biodegradation with IXPER 75C Calcium Peroxide was evaluated for the remediation of a BTEX contamination at an industrial site in Belgium.

Ten injection wells, divided over three injection screens, perpendicular to the direction of the groundwater flow and five monitoring wells with filter screen between 2 and 4 m bgl were installed on site. IXPER 75C Calcium Peroxide was injected in each injection well as a slurry. During two other injection events, water was injected to improve the distribution of oxygen in the aquifer.

Baseline monitoring showed concentrations of <0.2 to 150,000 µg/L BTEX in the monitoring and injection wells. This high variation in BTEX concentrations can be explained by the soil heterogeneity at an old industrial site (debris, foundations…).

After injection of IXPER 75C Calcium Peroxide, oxygen concentrations in all injection wells were >20 mg/L during at least 18 months, indicating extended release of oxygen. BTEX concentrations were monitored in two injection wells and decreased from 6,300 – 41,000 µg/L to 1 – 3 µg/L.

In one monitoring well with a relatively high BTEX concentration (35,000 µg/L), this concentration significantly decreased to 11,000 µg/L. In a monitoring well with 81,000 µg/L BTEX, no significant BTEX degradation was observed, but the phenol index increased from 68 to 290 µg/L. However, no significant increase in oxygen concentration was measured in both monitoring wells. This can possibly be explained by fast oxygen consumption at high contaminant concentrations. In two monitoring wells with relatively low BTEX concentrations (<0.2 to 5,100 µg/L), oxygen concentrations of 6 to 8 mg/L were detected and BTEX concentration decreased from 5,100 to 1,900 µg/L.

These observations demonstrate successful stimulated aerobic biodegradation of BTEX with IXPER 75C Calcium Peroxide. Furthermore, IXPER 75C Calcium Peroxide showed extended release of oxygen during at least 18 months.

IXPER 75C Calcium Peroxide

The limiting factor of aerobic biodegradation in soil is often the availability of oxygen. Aerobic biodegradation can be stimulated by increasing the oxygen concentration in groundwater to at least 4 mg/L.

The oxygen concentration in soil can be increased by air injection or by injection of oxygen releasing chemicals like magnesium peroxide, calcium peroxide or sodium percarbonate.

An overview of the properties of some oxygen releasing chemicals is given in Table 1.

Table 1. Properties of oxygen releasing chemicals (Solvay Chemicals)

Property	IXPER 35M Magnesium Peroxide	IXPER 75C Calcium Peroxide	Sodium Percarbonate
Chemical formula	MgO_2	CaO_2	$2\ Na_2CO_3.3\ H_2O_2$
Molecular weight (g/mol)	56	72	314
Purity (%)	>35	>75	>88
Impurity	MgO , other Mg cpds	$Ca(OH)_2$, $CaCO_3$	Na_2CO_3
pH[a]	10.3	11.9	10.4 - 10.6
Water solubility @ 20°C (g/L)	<0.1	<0.1	150
Chemistry in water	$Mg(OH)_2$, O_2	$Ca(OH)_2$, O_2	Na_2CO_3, H_2O_2, O_2
Available oxygen min (%)	10	17	13

IXPER 75C Calcium Peroxide generates the most oxygen (17%), compared to IXPER 35M Magnesium Peroxide (10%) and sodium percarbonate (13%). Calcium peroxide will slowly release oxygen due to its low water solubility (<0.1 g/L). In comparison, sodium percarbonate has a high water solubility (150 g/L) and oxygen will be released at a faster rate. Therefore, sodium percarbonate is probably less efficient for biodegradation compared to calcium peroxide.

The chemistry of calcium peroxide in water is given in reaction (1).

$$2\ CaO_2 + 2\ H_2O \rightarrow 2\ Ca(OH)_2 + O_2 \quad (1)$$

The rate of oxygen release is influenced by physico-chemical properties like pH and temperature. If calcium peroxide is exposed to a lower pH, it can generate H_2O_2 (reaction (2)).

$$CaO_2 + 2\ H^+ \rightarrow Ca^{2+} + H_2O_2 \quad (2)$$

Due to its high oxygen availability and slow but extended release of oxygen, calcium peroxide was chosen as oxygen releasing chemical in a pilot test to evaluate stimulated aerobic biodegradation for the soil remediation of a BTEX contamination at a site in Belgium.

Site description

The site is located in Belgium. The geology can be described as an upper layer (0 to 17 m bgl) of fine sand with loamy fraction. Between 4 and 17 m bgl, different sandstone layers are present at different depths. A clay layer is located from 17 to 22 m bgl. Groundwater flow velocity is 10 m/year. The direction of the groundwater flow is south to southeast.

Soil and groundwater are contaminated with BTEX due to historical production activities on site. The pilot test will focus on the BTEX contamination on top of the first sandstone layer at about 4 m bgl. Soil heterogeneity between 0 and 4 m bgl is high due to debris and foundations

Pilot test

Selection pilot test area

Since stimulated aerobic biodegradation will be used as a polishing step after excavation of the bulk contamination, the pilot test was performed on a less contaminated part of the site. Based on the soil investigation, an area with relatively low BTEX concentrations (<20 mg/L) was selected. However, baseline monitoring showed concentrations of <0.2 to 150,000 µg/L BTEX in the monitoring and injection wells. This high variation in BTEX concentrations can be explained by the soil heterogeneity at an old industrial site (debris, foundations…).

Pilot test set up

The pilot test set up is shown in Fig. 1. Ten injection wells, divided over three injection screens (screen 1: 5020, 5021, 5022; screen 2: 5023, 5024, 5025, 5026; screen 3: 5027, 5028, 5029), perpendicular to the direction of the groundwater flow, and five monitoring wells (5030, 5031, 601, 605 and 617) were installed on site with the filter on top of the first sandstone layer. The distance between the injection wells is 6 m. Injection wells of the first injection screen had a filter screen between 3 and 4 m bgl, while injection wells of the second and third injection screens had a filter screen between 2 and 4 m bgl. All monitoring wells have a filter screen between 2 and 4 m bgl.

IXPER 75C Calcium Peroxide was injected in each injection well as a slurry. Immediately after injection of the slurry, water was injected in each injection well to flush the filter. About three months after the IXPER 75C Calcium Peroxide injection, water was injected in each injection well. A high volume water injection was performed in injection wells 5027 and 5028 about four months after the IXPER 75C Calcium Peroxide injection. Both water injections were performed to improve the distribution of the released oxygen in the aquifer.

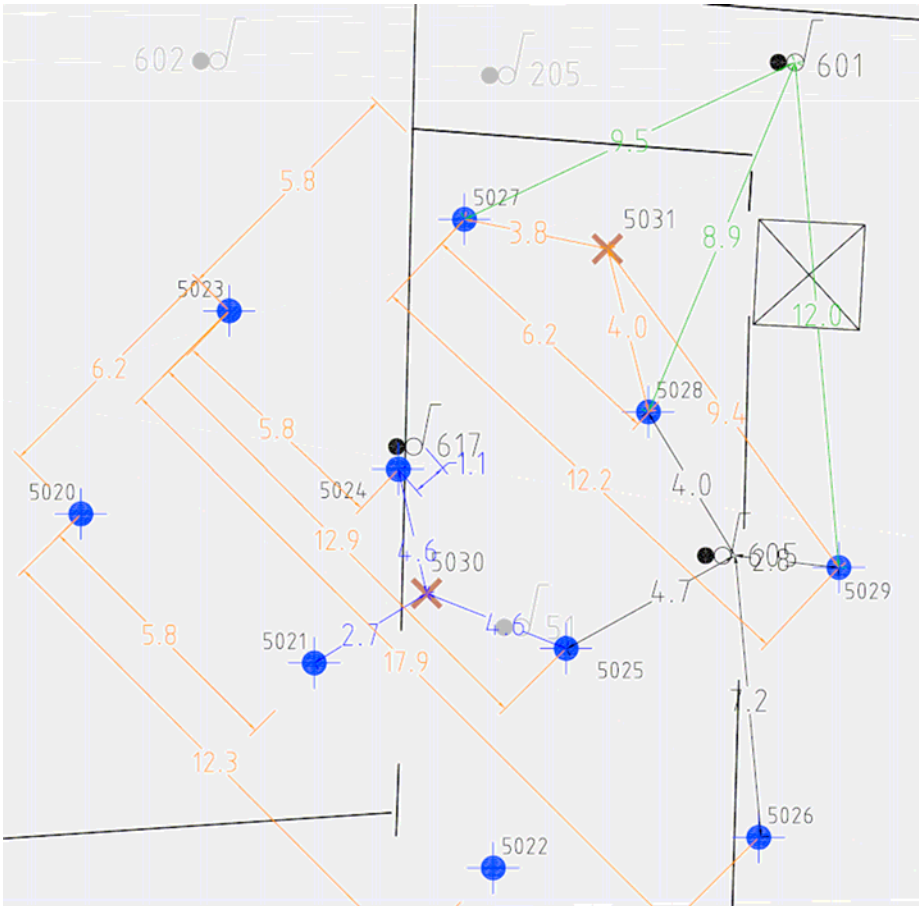

Figure 1. Pilot test set up with injection wells 5020, 5021, 5022, 5023, 5024, 5025, 5026, 5027, 5028 and 5029 and monitoring wells 5030, 5031, 601, 605 and 617. Distance beween wells in m.

Results and discussion

The BTEX concentration in injection wells 5022 and 5024 and monitoring wells 5031, 605 and 617 is shown in Fig. 2.

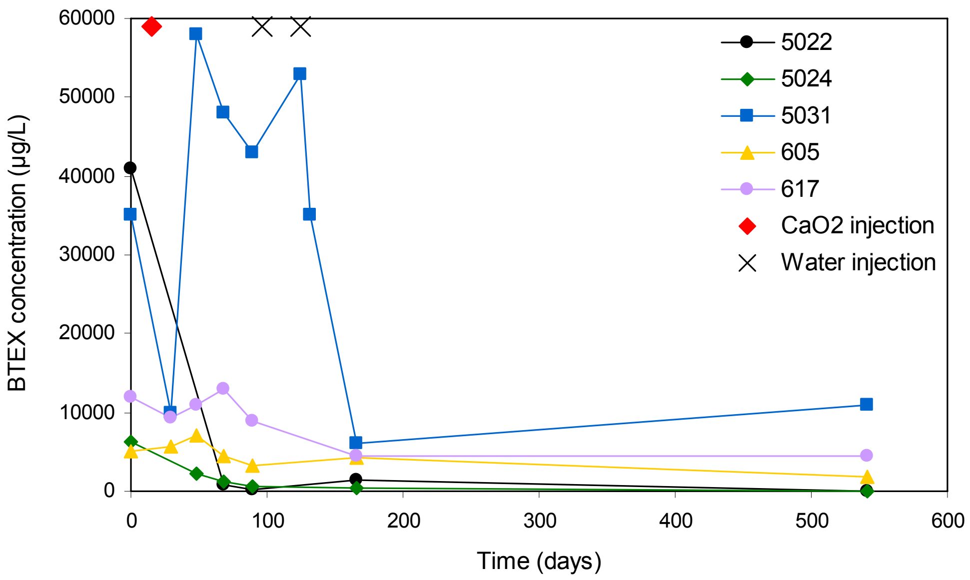

Figure 2. BTEX concentration in injection wells 5022 and 5024 and monitoring wells 5031, 605 and 617 during the pilot test with one IXPER 75C Calcium Peroxide injection and two water injections.

<u>Injection wells</u>

After injection of IXPER 75C Calcium Peroxide, pH increased from pH 7 to pH 12 – 13. This high pH value is in accordance with the pH of a suspension of IXPER 75C Calcium Peroxide (Table 1). The oxygen concentrations in all injection wells increased from 2 – 3 mg/L to >20 mg/L. Oxygen concentrations in most injection wells were still >20 mg/L 18 months after calcium peroxide injection, indicating extended release of oxygen during at least 18 months.

BTEX concentrations were monitored in the injection wells 5022 and 5024 and decreased from 6,300 – 41,000 µg/L to 490 – 1500 µg/L five months after Ca peroxide injection and even further to 1 – 3 µg/L 18 months after Ca peroxide injection. These results indicate stimulated aerobic biodegradation in the injection wells.

<u>Monitoring wells</u>

Monitoring well 5031 showed a significant BTEX degradation from 35,000 µg/L to 6,000 µg/L five months after IXPER 75C Calcium Peroxide injection with rebound to 11,000 µg/L 18 months after calcium peroxide injection. Significant BTEX degradation was only observed after the second water injection. Since the second water injection focused on injection wells 5027 and 5028 and monitoring well 5031 is located about 4 m from injection wells 5027 and 5028, these results could indicate that injection of water improved the distribution of oxygen and subsequent BTEX biodegradation in the aquifer.

A significant BTEX degradation was not observed in monitoring well 5030, possibly due to the very high BTEX concentration (81,000 µg/L). However, this monitoring well showed a significant increase of the phenol index from 68 to 290 µg/L, indicating aerobic biodegradation.

Increased oxygen concentrations were not observed in monitoring wells 5030 and 5031. This can be explained by fast oxygen consumption at high contaminant concentrations.

In monitoring well 605, the BTEX concentration decreased from 5,100 µg/L to 1,900 µg/L 18 months after IXPER 75C Calcium Peroxide injection, indicating stimulated aerobic biodegradation of BTEX. Monitoring well 601 contained no BTEX contamination (<0.2 µg/L). In monitoring wells 601 and 605 with no or relatively low BTEX concentrations, oxygen concentrations of 6 to 8 mg/L were measured about one month after the first water injection, indicating that injection of water improved the distribution of oxygen in the aquifer.

In monitoring well 617 at 1.1 m of injection well 5024, the presence of calcium peroxide was observed, demonstrating an injection radius of influence of at least 1.1 m. The BTEX concentration decreased from 12,000 µg/L to 4,400 µg/L.

Conclusion

The pilot test demonstrated successful stimulated aerobic biodegradation of BTEX with IXPER 75C Calcium Peroxide. This product showed extended release of oxygen during at least 18 months. However, water solubility of IXPER 75C Calcium Peroxide is low (<0.1 g/L) and therefore, homogeneous distribution of injected calcium peroxide in an aquifer can be difficult. Therefore, the bulk contamination in soil will first be excavated during full scale remediation of the site. Afterwards, IXPER 75C Calcium Peroxide will be mixed with the soil to get a homogeneous distribution of the product. IXPER 75C Calcium Peroxide will also be injected around the excavated areas.